

STUDIES ON IDENTIFYING THE TYPE AND RATE OF CORROSION OF METALLIC MATERIALS IN GEOTHERMAL PLANTS. CASE STUDY

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Abstract

The present paper presents the experiments made for the determination of the corrosion typ and rates for four types of carbon steels (frequently used in the installations for the transportation of the geothermal water), in the case of well 4797 Oradea. Gravimetric methods have been used for the determination of the corrosion rate. The sampled was observed with the help of the metallographic microscope.

Key words: aggressive species, corrosion speed.

INTRODUCTION

The chemical species that are usually present in geothermal waters, and that can cause corrosion (especially upon the carbon steel) are: oxygen (it appears in the usage installations of the geothermal waters through aeration, as a consequence of some operations that cannot be avoided: opening-closing, valve isolation, etc), hydrogen ions, chlorides, sulphides, carbon dioxide (Das G.S., Khanna A.S., 2004), ammonium ion, sulphate ion (that interfere both in the corrosion in the well and in the corrosion of the transport and usage installations).

MATERIAL AND METHODS

The results achieved in the laboratory offer indicative information upon the behaviour of a metal to corrosion in the given environment (Petr Brož, 2003). The real conditions inside an installation are more difficult to simulate, therefore, the final conclusions may be drawn only after some field measurements have been made (Malik A., 1999, Natesan M., 2008). The most frequent methods used on the site are: monitoring and control of the machinery, if it is possible through non-destructive methods, the quantization of metals from the corrosive environment and the analysis of the corrosion products, the usage of samples for the determination of the mass loss or the modification of some mechanical characteristics, metallographic examination to highlight the intercrystalline corrosion, electrochemical and electrical methods (Kovacevic Z., 2011)

The proposed quantitative method was that of the mass loss, having in view that it offers fairly accurate results, and the field conditions don't allow the usage of some electrochemical methods that involve electronic devices (Andrade C. Martinez I., 2003). The corrosion rate was expressed by the help of the gravimetric and penetration indices. Four types of steels, that are currently used as materials for the pipe and heat exchanger's construction, have been chosen as metallic materials for testing. They are: OLT 35 K, OLT 45 K, OLT 35 R and OLT 45 R. The samples used within the experiment have the form of rings. They have been cut unprotected, without soldering, cold-drawn from the steel pipe. The samples subjected to corrosion have the following dimensions: exterior diameter = 20 mm, interior diameter = 16 mm, ring height = 10 mm, wall thickness = 2 mm. The rings have been introduced in an exterior coat through which the geothermal fluid passes and it is foreseen with a thread at both ends, so that the whole assembly can be fit up on the chosen place in the installation. The connecting pipes have been made so that the placement of the samples and their sequential extraction could not restrain the good circulation of the geothermal fluid in the installation, where it was attached. During the experiment, the installation was permanently full of water in circulation. The installation that was used during the experiments can be seen in *figure 1, a and b*.



Fig. 1.a Coated Device



Fig. 1.b Uncoated Device

For the metallographic analysis, the corroded rings samples from tronson III and the control rings have been introduced in resin and metallographically processed thorough polishing with abrasive paper and mechanical smoothing till mirror-finishing, on felt with one-micron diamond powder (Suess S. J., 2002). The samples have been examined with a metallographic microscope, first macroscopically to highlight some possible geometrical changes. The samples have been furtherly attacked

with Nital (solution of nitric acid in alcohol) to highlight the microstructure and marginal areas. These observations offered information upon the type of corrosion: uniform, pointed or intercrystalline corrosion, as well as information regarding the intensity of the phenomenon

To study the phenomena that take place in the transport system of the thermal water, we interposed the experimental device on a by-pass of the pipe that leads the thermal water from the degasers, through pumping, to the entrance in the heat exchangers, as it can be seen in *figure 2*.



Fig. 2. Positioning of the experimental device in the installation

During the experiment, the device was full of water in circulation.

RESULTS AND DISCUSSION

The corrosion products were observed with a surface metallographic microscope CITIVAL, for macrosections. The achieved image is presented in *figure 3*.



Fig. 3. Aspect of the surface covered with corrosion products

The metallic material that reached the highest corroding rate is OLT 45 R in the water of the well 4797. The sample from by-pass III, made up of this material, was observed with the help of the metallographic microscope.

The microstructure of the marginal areas was highlighted by attacking the sample with a solution of 1% Nital (Cook R.,1998). The metallographic structures are ferrito-perlitic, mostly ferrite. The steel granulation is of 0.02 mm. After the metallographic analysis, a corrosion process through pits have started, on a depth up to 0.1 mm, in the marginal area. (figure 4)

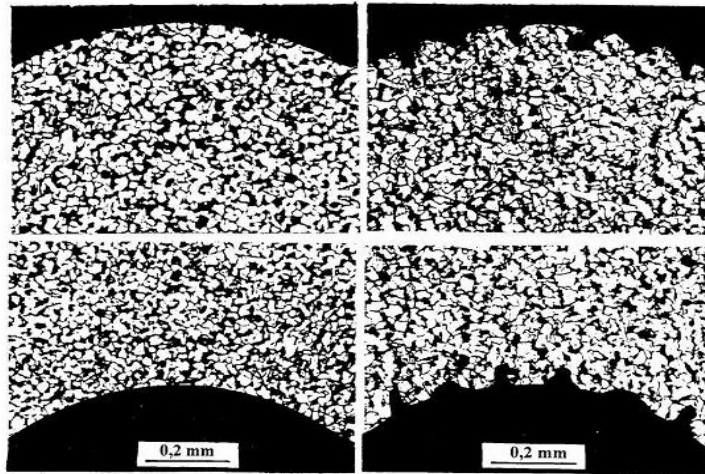


Fig. 4. Image of pointed corrosion

The masses of the depositions and the corrosion rates expressed through the penetration index, for the four types of steel, according to time, are presented in *tables 1-4*.

Table 1

Deposition mass and corrosion rates for OLT 35K

Time range (days)	Deposition mass (g)	Corrosion rate (mm/year)
32	0,0450	0,753
69	0,4659	0,632
101	0,5028	0,513

Table 2

Deposition mass and corrosion rates for OLT 35R

Time range (days)	Deposition mass (g)	Corrosion rate (mm/year)
32	0,0311	0,208
69	0,4574	0,575
101	0,4593	0,617

Table 3

Deposition mass and corrosion rates for OLT 45K

Time range (days)	Deposition mass (g)	Corrosion rate (mm/year)
32	0,0435	0,359
69	0,5357	0,530
101	0,3749	0,821

Table 4

Deposition mass and corrosion rates for OLT 45R

Time range (days)	Deposition mass (g)	Corrosion rate (mm/year)
32	0,0344	0,417
69	0,4449	0,587
101	0,7362	0,977

In the case of geothermal waters, the presence of chloride ions doesn't have to be neglected. They favour the dissolution of some possible protecting layers. A crust sampled from the geothermal environment and analyzed by X-rays show how the concentration of chloride ions increases according to the movement from the interface crust-solution towards the interface crust metal. This confirms the importance of the chlorides in the activation of the corrosion (Otsuki N., Nishida T., Madlangbayan M., 2007). The interior layer is made up of iron salts as $\text{FeO}(\text{OH}_3\text{Cl})$, $\text{FeCl}_2 \cdot n\text{H}_2\text{O}$, $\text{Fe}_2(\text{OH})_3\text{Cl}$, FeCO_3 and Fe_xS_y in small quantity (Andritsos N., Karabelas A.J., 1989). The second layer is made up of 80% iron sulphide under the form of grids (mackinawite). There are also other sulphides, such as pyrite and marcasite. Some studies made upon the behaviour of carbon steel and stainless steels suggest even correlations of mathematical origin between the corrosion rates (determined through the method of mass loss measurement) and the concentration of the chloride ions. In general, the formed crusts, having the standard potential higher than that of the metal can contribute to the intensification of the corrosion kinetics. There are studies which show that the iron sulphides are cathodic parts that influence mainly the discharge of the hydrogen ion. The high concentrations of the carbon dioxide actively takes part in the process of corrosion. The corrosion products are very soluble (e.g. ferrous bicarbonate) or less soluble (e.g. ferrous carbonate). There was noticed the formation of some cavities on the separation limit between the ferrous carbonate and the uncovered surface, because its structure is not homogenous.

CONCLUSIONS

Despite of the high quantities of deposits on the sample surface, the corrosion rate is important. This fact is due to the possibility as corrosion to

take place even under the deposits. They are not adherent on the metal's surface, and for this reason the corrosion can be even increased as a consequence of the environmental differences with whom the metallic parts come into contact. The intensification of the reduction reactions is favoured on the covered surfaces and the intensification of the oxidation reaction is favoured on the uncovered surfaces .

The metallic material that reached the highest corroding rate is OLT 45 R in the water of the well 4797. The sample from by-pass III, made up of this material, was observed with the help of the metallographic microscope. No geometrical changes of the sample during the experiments have been recorded. After the metallographic analysis, a corrosion process through pits have started, on a depth up to 0.1 mm, in the marginal area.

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